Journal of Fluorine Chemistry 130 (2009) 332–335

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Direct addition of fluorine to arylacetylenes

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ARTICLE INFO

Article history:
Received 14 October 2008
Received in revised form 15 December 2008
Accepted 18 December 2008
Available online 27 December 2008

Keywords:
F_2
Acetylenes
Direct fluorination
Aryltetrafluoroethanes

ABSTRACT

Under suitable conditions elemental fluorine can be added across the carbon–carbon triple bond of arylacetylenes forming tetrafluoroethane derivatives – $ArCF_2CF_2R$ – in good yields.

1. Introduction

Today there is no need to elaborate on the importance of the fluorine atom in organic chemistry, especially in the physical and biological fields. There are numerous examples of fluorine containing compounds which have found many applications in medicinal and material chemistry [1,2]. Recently, it was reported that the introduction of tetrafluoroethane bridges (CF_2CF_2) to the structure of liquid crystals yields new classes of materials with improved properties for applications in active matrix liquid crystal display (LCDs) [3]. Furthermore, bridge-fluorinated octafluoro[2.2]paracyclophane was found to be a very useful chemical vapor deposition (CVD) precursor of a family of thin film polymers known as parylenes [4].

Addition of halogens to π centers is almost as old as chemistry itself. The terms halogens in this context, however, was reserved almost exclusively to Cl_2, Br_2 and occasionally also to XF (X = Br, I, OH) [5–7] but almost never to F_2. Merritt was the first to add F_2 to some double and triple bonds [8], but his technique was such that nobody could repeat the experiments in the last 40 years. During this period, many believed that using elemental fluorine for organic synthesis is an exercise in futility since this halogen is so reactive that inevitably the reactions were supposed to be destructive. Slowly, but steadily, we and others have shown that under the right conditions this element can become very potent, and yet very selective, both in cases of employing it directly [9–12] or in using it as a tool for constructing other fluorine containing reagents [13,14]. In the past we have developed a methodology for adding fluorine across double bonds [15], but adding it across triple ones was more challenging. Compounds with the general formula of $ArCF_2CF_2Ar'$ were achieved, for example, by preparing 1,2-difluorostilbenes from tetrafluoroethylene and only then treated with F_2 to form the tetrafluoro derivatives. Direct addition of this halogen to triple bonds was described to give "complicated mixtures" [16]. Another indirect approach was to react Deoxofluor® with some benziles [17] or use combination of reagents such as nitrosonium tetrafluoroborate ($NO^+BF_4^-$) and pyridinium polyhydrogen fluoride (PPHF) [18]. We report here of our attempts to add F_2 across triple bonds toward producing the tetrafluoroethanes derivatives in a direct one-step reaction.

2. Results and discussion

When diluted fluorine (3–10% F_2 in N_2) was bubbled slowly through a cold solution (−78 °C) of diphenylacetylene (**1a**) in a mixture of $CHCl_3$/$CFCl_3$/EtOH as a solvent, 1,2-diphenyltetrafluoroethane (**2a**) [19] was formed in 75% yield (Scheme 1).

Consequently, a series of substituted arylacetylenes with either electron donating or withdrawing groups were allowed to react with elemental fluorine under similar reaction conditions. 1-Methoxy-4-(phenylethynyl)benzene (**1b**) gave 1-methoxy-4-(1,1,2,2-tetrafluoro-2-phenylethyl)benzene (**2b**) [18] in 65% yield and 1-ethyl-4-(phenylethynyl)benzene (**1c**) was converted to the corresponding 1-ethyl-4-(1,1,2,2-tetrafluoro-2-phenylethyl)benzene (**2c**) in 70% yield. In both cases, despite the presence of activated rings toward electrophilic attack, we have not found

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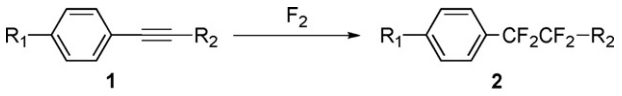
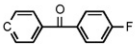
doi:10.1016/j.jfluchem.2008.12.009



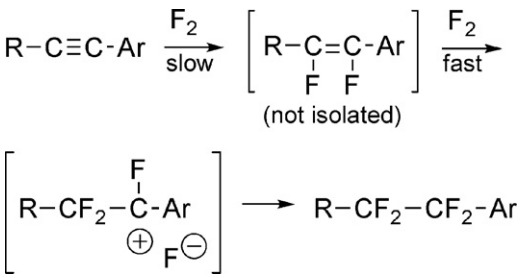
1 2

a	R_1 = H; R_2 = Ph	75%
b	R_1 = H; R_2 = 4-OMe-C_6H_4	65%
c	R_1 = H; R_2 = 4-Et-C_6H_4	70%
d	R_1 = H; R_2 = 4-Cl-C_6H_4	70%
e	R_1 = H; R_2 = 	70%
f	R_1 = H; R_2 = 4-CN-C_6H_4	75%
g	R_1 = H; R_2 = 4-NO_2-C_6H_4	70%
h	R_1 = Br; R_2 = 4-Br-C_6H_4	65%
i	R_1 = H; R_2 = Pr	45%
j	R_1 = Br; R_2 = COOMe	40%

Scheme 1. Adding fluorine to acetylenes.

aromatic substitution products as with other electrophilic regents derived from F_2 [20–22], indicating that the triple bond reacts faster with F_2 than the benzenoidic aromatic π electrons. Halogen possessing derivatives such as 1-chloro-4-(phenylethynyl)benzene (**1d**) or 4-(phenylethynyl)-4′-fluorobenzophenone (**1e**) behaved similarly forming 1-chloro-4-(1,1,2,2-tetrafluoro-2-phenylethyl)benzene (**2d**) and 1-(*p*-fluorobenzophenone)-2-phenyl-1,1,2,2-tetrafluoroethane (**2e**) both in 70% yield without any halogen exchange. Strong electron-withdrawing moieties such as cyano, or nitro groups found in 4-(phenylethynyl)benzonitrile (**1f**) and 1-nitro-4-(phenylethynyl)benzene (**1g**) did not alter the reaction course either, and the fluorine attacked selectively the carbon–carbon triple bond, producing the desired 4-(1,1,2,2-tetrafluoro-2-phenylethyl)benzonitrile (**2f**) in 75% yield and 1-nitro-4-(1,1,2,2-tetrafluoro-2-phenylethyl)benzene (**2g**) in 70% yield. Disubstituted 1,2-bis(4-bromophenyl)ethyne (**1h**) was also successfully fluorinated to the corresponding 1,2-bis(4-bromophenyl)-1,1,2,2-tetrafluoroethane (**2h**) in 65% yield [17]. The reaction is not limited to tolanes although the best results were associated with this family. We found that monoarylacetylenes such as 1-pentynylbenzene (**1i)** and methyl phenylpropiolate (**1j**) did react with elemental fluorine to produce the desired (1,1,2,2-tetrafluoropentyl)benzene (**2i**) and methyl 2,2,3,3-tetrafluoro-3-phenylpropanoate (**2j**) products. The yields of these reactions were somewhat lower (45% and 40%, respectively) and the by-products formed made analytical purification of the tetrafluoro compounds extremely difficult. Moving a step further, to dialkylacetylenes, proved to be completely impractical as only minute amounts of the desired tetrafluoro products were detected along with numerous other by-products.

Although there is no profound effect on the reaction by the ring substitution, we believe that a radical mechanism is not likely. When the reaction was performed in the presence of radical chain scavengers such as 1,3-dinitrobenzene or oxygen, the fluorine was added across the triple bond with the same efficiency as when such scavengers were not present. In addition, it is clear that the presence of an alcohol such as ethanol, is mandatory since in its absence a complicated mixture of fluorinating products was obtained. Leaving us with the ionic reaction prospect means that one of the roles of ethanol, or methanol for that matter, is to serve as an acceptor for the developing fluoride anion through hydrogen



Scheme 2. The proposed mechanism of the addition of F_2 to arylacetylenes.

bonding lowering the transition state and enabling the addition reaction to occur. As shown in the past, such a chain of events is essential for ionic reactions involving F_2 [23].

The mechanism outlined above may serve as a guideline for the addition reaction described in this work. Despite the high probability that the creation of the tetrafluoro derivative is a two-step reaction, we were not able to detect the difluoroolefin intermediate. This is rationalized by the assumption that the difluoroolefin reacts faster than the starting acetylene with F_2 since the resulting carbocation α to the CF_2 moiety should form a relatively unstable ions which collapse fast. When two vicinal aryl groups are present, the above carbocation is stabilized enough to react with the counter fluoride ion to form the tetrafluoroethane product (Scheme 2) [24]. When such stabilization is weakened, as in mono aryl or lacking, as in alkylacetylenes, the unstable carbocation may turn to other collapsing options such as fast rearrangements. This may lead to creation of several secondary carbocations along the chain, which apart from their own reactions with F_2, can also result in a host of additional unsaturated centers all of which react fast with the halogen to produce many fluorine containing products, lowering the yield of the reaction or rendering it impractical.

3. Experimental

^{1}H NMR spectra were recorded using a 200 MHz spectrometer with $CDCl_3$ as a solvent and Me_4Si as an internal standard. The ^{19}F NMR spectra were measured at 188.1 MHz with $CFCl_3$, serving as an internal standard. The proton broad-band decoupled ^{13}C NMR spectra were recorded at either 50.2 MHz or at 100.5 MHz. Here too, $CDCl_3$ served as a solvent and Me_4Si as an internal standard. MS was measured under EI, or ESI-QqTOF conditions. In case these methods could not detect the molecular ion, we have successfully used the Amirav's supersonic GC–MS developed in our department. The main feature of this method is to provide electron ionization while the sample is vibrationally cooled in a supersonic molecular beam. This considerably enhances the relative abundance of molecular ions [25,26]. Silica gel 60H (Merck) and petroleum ether/ethyl acetate were used for flash chromatography. As mentioned above we were unable to obtain analytically pure samples of compounds **2i** and **2j** and used isotope abundance analysis to confirm the structure. This analysis confirmed the proposed elemental formulas as it ranked them at the first place and hence as the best choice with very good matching factors of better then 860 (out of 999) [27].

3.1. General fluorination procedure

Fluorine is a strong oxidant and corrosive material. In organic chemistry, it is mostly used after dilution with nitrogen or helium. Such dilution can be achieved by using either an appropriate cooper or monel vacuum line constructed in a well-ventilated area or simply purchasing prediluted fluorine. A detailed description for

simple setup had appeared in the past [28]. The reactions themselves can be carried out in regular glassware. If elementary precautions are taken, work with F_2 is simple and we have had no bad experiences working with it.

The reactions were usually carried out on scales of 1–5 mmol acetylene derivatives, monitored by GC on a 3% SE-30 column, and usually stopped when conversion reached about 95%. Fluorine, at a concentrations of 3–10% in N_2, was slowly passed through a cold (−78 °C) and vigorously stirred solution of the arylacetylene dissolved in 100 mL of $CFCl_3$, 125 mL $CHCl_3$ and 25 mL of EtOH. An efficient mixing is achieved by using a vibromixer, which also ensures a fine dispersion of the gas bubbles. The term "worked up as usual" means stopping the reaction by pouring it into 200 mL water, washing the organic layer with $NaHCO_3$ solution followed by water until neutral, drying the organic layer over $MgSO_4$, and finally evaporating the solvent. The crude product was usually purified by vacuum flash chromatography using silica gel 60-H (Merck) or by recrystallization.

3.2. Preparation of starting materials

Substituted diarylacetylenes were prepared using known procedures mainly by reacting cuprous phenyl acetylide with variously substituted iodoarenes in refluxing pyridine [29].

1,2-Diphenyltetrafluoro ethane (2a) [19] was prepared from **1a** (0.92 g) as described above. After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using petroleum ether as eluent. The tetrafluoro product was obtained as white crystals in 75% yield: 0.98 g; mp: 120.3–121.0 °C; ^{1}H NMR 7.40–7.48 ppm (10H, m); ^{13}C NMR 116.8 (tt, $^1J_{C-F}$ = 253 Hz, $^2J_{C-F}$ = 36 Hz), 127.1 (t, J_{C-F} = 4 Hz) 128.2, 131.1 ppm; ^{19}F NMR −112.2 ppm (4F, s); MS (EI) (*m*/*z*) (M)$^+$: 254.

1-Methoxy-4-(1,1,2,2-tetrafluoro-2-phenylethyl)benzene (2b) [18] was prepared from **1b** (0.30 g) as described above. After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using 10% ethyl acetate in petroleum ether as eluent. The tetrafluoro product was obtained as white crystals in 65% yield: 0.26 g; mp: 38.9–39.2 °C; ^{1}H NMR 3.84 (3H, s), 7.32–7.47 ppm (9H, m); ^{13}C NMR 55.4, 113.5, 116.8 (tt, $^1J_{C-F}$ = 251 Hz, $^2J_{C-F}$ = 36 Hz), 116.9 (tt, $^1J_{C-F}$ = 251 Hz, $^2J_{C-F}$ = 36 Hz), 123.0 (t, J_{C-F} = 25 Hz), 126.9 (t, J_{C-F} = 6 Hz), 128.4, 128.9 (t, J_{C-F} = 6 Hz), 131.2, 131.7 (t, J_{C-F} = 18 Hz), 161.7 ppm; ^{19}F NMR −111.2 (2F, s), −112.3 ppm (2F, s); HRMS (CI) (*m*/*z*) calcd for $C_{15}H_{12}F_4O$ = 285.0902 (M + H)$^+$, found: 285.0903.

1-Ethyl-4-(1,1,2,2-tetrafluoro-2-phenylethyl)benzene (2c) was prepared from **1c** (0.50 g) as described above. After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using petroleum ether as eluent. The tetrafluoro product was obtained as white crystals in 70% yield: 0.48 g; mp: 69.3–70.1 °C; ^{1}H NMR 1.25 (3H, t, *J* = 8 Hz), 2.69 (2H, q, *J* = 8 Hz), 7.22–7.24 (2H, m), 7.35–7.47 ppm (7H, m); ^{13}C NMR 15.4, 28.8, 116.8 (tt, $^1J_{C-F}$ = 253 Hz, $^2J_{C-F}$ = 36 Hz), 116.9 (tt, $^1J_{C-F}$ = 252 Hz, $^2J_{C-F}$ = 36 Hz), 127.1, 127.8, 128.2, 128.3 (t, J_{C-F} = 25 Hz), 130.9, 131.2 (t, J_{C-F} = 25 Hz) 147.5 ppm; ^{19}F NMR −111.7 (2F, s), −112.2 ppm (2F, s); The usual MS methods fail to show any molecular peak. However, using Amirav's method revealed a strong molecular ion peak of *m*/*z* 282 (M)$^+$. Anal. Calcd for $C_{16}H_{14}F_4$: C, 68.08; H, 5.00; F, 26.92. Found: C, 67.92; H, 4.88; F, 27.15.

1-Chloro-4-(1,1,2,2-tetrafluoro-2-phenylethyl)benzene (2d) was prepared from **1d** (0.95 g) as described above. After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using petroleum ether as eluent. The tetrafluoro product was obtained as white crystals in 70% yield: 0.90 g; mp: 49.9–50.5 °C; ^{1}H NMR 7.39–7.47 ppm (9H, m); ^{13}C NMR 116.5 (tt, $^1J_{C-F}$ = 253 Hz, $^2J_{C-F}$ = 37 Hz), 116.6 (tt, $^1J_{C-F}$ = 253 Hz, $^2J_{C-F}$ = 37 Hz), 127.1 (t, J_{C-F} = 6 Hz), 128.3, 128.6, 129.2 (t, J_{C-F} = 24 Hz), 130.7 (t, J_{C-F} = 24 Hz), 131.2, 137.5 ppm; ^{19}F NMR −112.3 (2F, s), −112.3 ppm (2F, s); The usual MS methods fail to show any molecular peak. However, using Amirav's method revealed a strong molecular ion peak of *m*/*z* 288 (M)$^+$. Anal. Calcd for $C_{14}H_9F_4Cl$: C, 58.25; H, 3.14. Found: C, 58.36; H, 2.88.

1-(p-Fluorobenzophenone)-2-phenyl-1,1,2,2-tetrafluoroethane (2e) was prepared from **1e** (0.54 g) as described above. After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using 5% ethyl acetate in petroleum ether as eluent. The tetrafluoro product was obtained as white crystals in 70% yield: 0.48 g; mp: 174.9–175.7 °C; ^{1}H NMR 7.19 (2H, t, *J* = 8 Hz), 7.45–7.51 (5H, m), 7.61 (2H, d, *J* = 8 Hz), 7.81 (2H, d, *J* = 8 Hz), 7.84–7.88 ppm (2H, m); ^{13}C NMR 115.9 (d, J_{C-F} = 22 Hz), 116.4 (tt, $^1J_{C-F}$ = 252 Hz, $^2J_{C-F}$ = 36 Hz), 116.7 (tt, $^1J_{C-F}$ = 253 Hz, $^2J_{C-F}$ = 36 Hz), 127.1 (t, J_{C-F} = 6 Hz), 127.3 (t, J_{C-F} = 6 Hz), 128.4, 129.5, 130.6 (t, J_{C-F} = 25 Hz), 131.3, 132.9 (d, J_{C-F} = 9 Hz), 133.3 (d, J_{C-F} = 3 Hz), 134.8 (t, J_{C-F} = 25 Hz), 139.9, 165.8 (d, J_{C-F} = 255 Hz), 194.5 ppm; ^{19}F NMR −105.4 (1F, s), −111.9 (2F, s), −112.3 ppm (2F, s); HRMS (ESI-Qq TOF) (*m*/*z*) calcd For $C_{21}H_{13}F_5O$ = 399.0778 (M + Na)$^+$, found: 399.0764. Anal. Calcd for $C_{21}H_{13}F_5O$: C, 67.02; H, 3.48; F, 25.24. Found: C, 66.95; H, 3.24; F, 25.15.

4-(1,1,2,2-Tetrafluoro-2-phenylethyl)benzonitrile (2f) was prepared from **1f** (0.50 g) as described above. After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using 1% ethyl acetate in petroleum ether as eluent. The tetrafluoro product was obtained as white crystals in 75% yield: 0.51 g; mp: 113.1–113.9 °C; ^{1}H NMR 7.43–7.75 ppm (9H, m); ^{13}C NMR 115.3, 115.9 (tt, $^1J_{C-F}$ = 253 Hz, $^2J_{C-F}$ = 35 Hz), 116.5 (tt, $^1J_{C-F}$ = 253 Hz, $^2J_{C-F}$ = 35 Hz), 117.9, 127.0 (t, J_{C-F} = 5.7 Hz), 128.5, 130.2 (t, J_{C-F} = 25 Hz), 131.5, 132.1, 135.6 ppm (t, J_{C-F} = 26 Hz); ^{19}F NMR −112.0 (2F, s), −113.0 ppm (2F, s); HRMS (CI) (*m*/*z*) calcd for $C_{15}H_9F_4N$ = 280.0749 (M + H)$^+$, found: 280.0742. Anal. Calcd for $C_{15}H_9F_4N$: C, 64.52; H, 3.25; N, 5.02. Found: C, 64.90; H, 3.09; N, 5.05.

1-Nitro-4-(1,1,2,2-tetrafluoro-2-phenylethyl)benzene (2g) was prepared from **1g** (1.10 g) as described above. After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using petroleum ether as eluent. The tetrafluoro product was obtained as white crystals in 70% yield: 1.03 g; mp: 91.3–92.0 °C; ^{1}H NMR 7.47–7.54 (5 H, m), 7.68 (2 H, d, *J* = 8 Hz), 8.3 ppm (2 H, d, *J* = 9 Hz); ^{13}C NMR 115.9 (tt, $^1J_{C-F}$ = 254 Hz, $^2J_{C-F}$ = 37 Hz), 116.5 (tt, $^1J_{C-F}$ = 254 Hz, $^2J_{C-F}$ = 37 Hz), 123.5, 123.8, 127.0 (t, J_{C-F} = 6 Hz), 128.5, 128.7, 129.4, 130.1 (t, J_{C-F} = 25 Hz), 131.5, 132.0, 132.4, 137.2 (t, J_{C-F} = 26 Hz) 149.7 ppm; ^{19}F NMR −111.9 (2F, s), −112.5 ppm (2F, s); The usual MS methods fail to show any molecular peak. However, using Amirav's method revealed a strong molecular ion peak of *m*/*z* 299 (M)$^+$. Anal. Calcd for $C_{14}H_9F_4NO_2$: C, 56.20; H, 3.03; F, 25.40; N, 4.68. Found: C, 55.95; H, 2.90; F, 25.90; N, 4.63.

1,2-Bis(4-bromophenyl)-1,1,2,2-tetrafluoroethane (2h) [17] was prepared from **1h** (0.80 g) as described above. After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using 5% ethyl acetate in petroleum ether as eluent. The tetrafluoro product was obtained as white solid in 65% yield: 0.63 g; mp: 98–100 °C; ^{1}H NMR 7.30 (4H, d, *J* = 9 Hz), 7.55 ppm (4H, d, *J* = 9 Hz); ^{13}C NMR 116.0 (tt, $^1J_{C-F}$ = 252 Hz, $^2J_{C-F}$ = 37 Hz), 125.8, 128.5, 129.2 (t, J_{C-F} = 26 Hz), 131.4 ppm; ^{19}F NMR −112.2 (2F, s).

(1,1,2,2-Tetrafluoropentyl)benzene (2i) was prepared from **1i**; oil, 45% yield: ^{1}H NMR 7.57–7.42 (5H, m), 2.00 (2H, t, *J* = 8 Hz), 1.62 (2H, sex, *J* = 8 Hz), 0.98 ppm (3H, t, *J* = 8 Hz); ^{13}C NMR 14.0, 14.4 (t, J_{C-F} = 4 Hz), 32.7 (t, J_{C-F} = 23 Hz), 116.8 (tt, $^1J_{C-F}$ = 251 Hz, $^2J_{C-F}$ = 35 Hz), 119.1 (tt, $^1J_{C-F}$ = 251 Hz, $^2J_{C-F}$ = 35 Hz), 126.9 (t, J_{C-F} = 6 Hz), 128.4, 130.9 ppm; ^{19}F NMR −110.7 (2F, s), −113.6 ppm (2F, t); The usual MS methods fail to show any molecular peak. However, using Amirav's method revealed a strong molecular ion

peak of m/z 220 $(M)^+$ with isotope abundance analysis matching factor of 867 out of 999 [27].

1-Methyl-(2,2,3,3-tetrafluoro-3-phenyl)propanoate (2j) was prepared from **1j**; oil, 40% yield: ^{1}H NMR 7.57–7.37 (5H, m), 3.91 ppm (3H, s); ^{13}C NMR 54.0, 109.4 (tt, $^1J_{C-F}$ = 260 Hz, $^2J_{C-F}$ = 39 Hz), 126.7 (t, J_{C-F} = 6 Hz), 128.6, 130.7, 131.6, 133.0, 154.5 ppm; ^{19}F NMR −112.0 (2 F, s), −119.0 ppm (2F, s); The usual MS methods fail to show any molecular peak. However, using Amirav's method revealed a strong molecular ion peak of m/z 236 $(M)^+$ with isotope abundance analysis matching factor of 960 out of 999 [27].

Acknowledgment

This work was supported by the USA-Israel Binational Science Foundation (BSF), Jerusalem, Israel.

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